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(54) **Refining assisting agent and refining method using the same**

Raffinierungshilfsmittel und Raffinierverfahren mit diesem

Agent auxiliaire au raffinage et procédé de raffinage l'utilisant

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(73) Proprietor: **JAPAN PMC CORPORATION**
Chuo-ku Tokyo 103 (JP)

(72) Inventor: **Hayashi, Jisuke**
Sapporo-shi, Hokkaido (JP)

(74) Representative: **von Fünér, Alexander, Dr. et al**
Patentanwälte v. Fünér, Ebbinghaus, Finck
Mariahilfplatz 2 & 3
D-81541 München (DE)

(56) References cited:
• **ABSTRACT BULLETIN OF THE INSTITUTE OF PAPER CHEMISTRY**, vol. 62, no. 6, December 1991, APPLETON US page 653; NICOL, S.: 'Life after death for empty shells.'
• **ABSTRACT BULLETIN OF THE INSTITUTE OF PAPER CHEMISTRY**, vol. 49, no. 11, May 1979, APPLETON US page 1045; ALLAN, G. G. ET AL: 'Chitosan - mediator for fiber-water interactions in paper.'
• **PATENT ABSTRACTS OF JAPAN** vol. 014, no. 559 (C-0787) 12 December 1990

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Description

This invention relates to a refining method using a novel refining assisting agent useful in refining wood chips or beating pulps.

Recently high-yield pulps have come to be commonly used as a main material for newsprint paper, magazine paper and low-grade printing paper. Typical examples of the high-yield pulp are refiner groundwood pulp (RGP) prepared by refining softwood chips with a disc refiner, thermomechanical pulp (TMP) prepared by treating heat-softened softwood chips with a disc refiner under a pressurized condition, chemiground pulp (CGP) and semichemical pulp (SCP) prepared by refining hardwood chips with a disc refiner after they are treated with sodium hydroxide or sodium sulfite.

These high-yield pulps have a problem that they are mechanically refined with a disc refiner in their preparation and demand more electric power than chemical pulps (CP), which is the most impedimental problem involved in the use of high-yield pulps. In the case of CP as well, beating of the pulp with a refiner is also normally carried out prior to the papermaking step for accelerating the swelling of the fibers and enhancing the bonding strength between the fibers. Here consumption of a large amount of energy is also a problem to be solved.

Studies in search of the additives useful for reducing power consumption in refining or beating of pulp have been conducted from the viewpoint of energy-saving. One of such studies, for instance, proposed direct addition of a dye Congo Red to the pulp, which remarkably reduces the power consumption in the beating. The use of Congo Red, however, is impracticable since it dyes the pulp red. The main object of the present invention is to provide a refining method using a novel refining assisting agent useful for reducing the power consumption in the production of high-yield pulp and in the beating of the pulp and consequently contributing to the energy saving as well as for enhancing the paper strength.

We have conducted extensive studies to solve the above-described problems, found that the use of a sulfonated chitosan having amino groups and sulfo groups as a refining assisting agent reduces the power consumption in the refining and beating of the pulp as well as enhances the paper strength of the obtained paper, and thus completed the present invention.

Accordingly, the present invention provides a method for refining woodchips or beating pulps, wherein a sulfonated chitosan, which is selectively sulfonated at the C3/C6 positions and not sulfonated at the C2 position NH_2 group, is used.

In a preferred embodiment of the present method a sulfonated chitosan, which is sulfonated at the C3 and the C6 positions and not sulfonated at the C2 position NH_2 -group is used.

In another preferred embodiment of the present method a sulfonated chitosan, which is sulfonated only at the C6 position and not sulfonated at the C2 position NH_2 -group, is used.

Details of the present invention will be made clear by the following description.

In the present invention, the term "refining (in a wide sense) assisting agent" means an agent which assists the mechanical refining (in a narrow sense) of wood chips in the preparation of high-yield pulps or assists the beating of pulps. The high-yield pulp is a pulp the preparation of which involves mechanical refining of wood chips with a disc refiner and exemplified by the above-mentioned RGP, TMP, CGP and SCP. The pulp to be beaten is a pulp which is beaten before made into paper and exemplified by the above-mentioned high-yield pulp, the chemical pulp (CP) such as sulfite pulp (SP), Kraft pulp (KP) and soda pulp (AP).

Sulfonated chitosan useful as a refining assisting agent in the refining or beating in accordance with the present invention is obtained by sulfonating chitosan which is obtained by deacetylating chitin contained in crustacean animals such as crabs, lobsters and insects, fungi. Conventional processes of sulfonating chitosan are described, for instance, in M. I., Wolfrom, T. M. Shen. Han, JACS 81, 1764 (1959). Sulfonated chitosan prepared by such conventional processes can be used but these processes involve a problem that sulfonation occurs at not only C3/C6 positions of chitosan but partially on the C2 position amino group, which hinders the amino group from being cationized.

In view of this fact, the following sulfonating process is preferred, which enables the selective sulfonation of the C3/C6 positions and does not impair the amino functionality of the chitosan. That is, it is preferred that the chitosan is subjected to the below-described pretreatment and then to a selective sulfonation at the C3/C6 positions using a sulfonating agent of SO_3 -DMF complex or ClASO_3 -DMF complex in a non-polar solvent.

In the above-mentioned preferred process, a pretreatment comprising the following steps must be effected:

- (1) Dissolving chitosan in an acetic acid solution having a concentration of 1-2% or swelling chitosan to a large or extreme extent in an acetic acid solution having a concentration of 1-2%.
- (2) Regenerating chitosan with an alkaline aqueous solution.

Ordinary alkalis such as NaOH , Na_2CO_3 , KOH are usable in this step. NaOH is the most preferable. The regeneration of dissolved chitosan can be effected by neutralisation-precipitation and the regeneration of swollen chitosan can be effected by "deswelling" or removing the excess liquid therefrom.

- (3) Washing the thus regenerated chitosan with water and then with alcohol.

Suitable alcohols include methanol and ethanol

(4) Immersing the washed chitosan in a polar solvent and pressing the solvent out of the same to replace the alcohol with a specific polar solvent.

Polar solvents suitable for this purpose include dimethylformamide (DMF) and dimethyl sulfoxide (DMSO).

The foregoing pretreatment enables the subsequent sulfonating step to proceed like a homogeneous phase reaction though it is, in fact, substantially a heterogeneous phase reaction.

Without the above-described pretreatment, the hetero-geneous-phase sulfonation reaction using a solvent such as benzene and toluene, which does not dissolve the reaction product (sulfonated chitosan) proceeds from the surface of the solid and gives water-soluble sulfonated chitosan of only a few % of the starting material even after 24 hour reaction.

In contrast, when chitosan has been subjected to the pretreatment prior to the heterogeneous-phase sulfonation reaction; sulfonated chitosan can be obtained in an about 100% yield by one-hour reaction at room temperature.

Furthermore, this pretreatment provides another effect that the quaternized amino groups remain unchanged after they undergo a neutralization step and the amino groups are protected from sulfonation, which enables the selective sulfonation of the C3/C6-position hydroxyl groups and eliminates the necessity of recovering of the C2 position amino groups by desulfonation.

Sulfonation can be effected by using SO_3 -DMF complex or ClHSO_3 -DMF complex as a sulfonating agent and a non-polar solvent as solvent, at a temperature of 0-100°C, preferably 5-80°C, for 0.1-48 hours under agitation.

Further selectivity in the reaction (i. e. selective sulfonation only at the C6-position or sulfonation wherein the C3/C6-positions are sulfonated in a desired ratio) can be attained by selecting these reaction conditions.

That is, we found that the selective reaction at the C6-position can be attained by conducting the reaction at a relatively high temperature and a reaction at a relatively low temperature for a long time improves the sulfonation degree at the C3-position.

SO_3 -DMF complex can be prepared by allowing SO_3 to be absorbed and dissolved in DMF. ClHSO_3 -DMF complex can be prepared by dropwise addition of chlorosulfonic acid (ClHSO_3) to DMF.

Preferable non-polar solvents are aromatic solvents, benzene or toluene being most preferred.

In the sulfonation step of this process, hydroxyl groups at the C3/C6-positions are selectively sulfonated. Since the produced water-soluble sulfonated chitosan does not dissolve in a non-polar solvent such as benzene, it can be separated by filtration. Furthermore, since the reaction does not involve formation of sodium sulfonate, washing of sulfonated chitosan can be easily effected by a small amount of methanol.

In addition, the filtrate can be recycled by replenishing SO_3 or ClHSO_3 to form DMF-complex. Thus the process reduces the amount of DMF, methanol and sulfonating agents used in the process and, therefore, brings about economical advantages.

A filtration step follows the sulfonation step and the filtrate comprising the unreacted sulfonating agent, polar and non-polar solvents is recycled and the residue comprising sulfonated chitosan (object compound) and a slight amount (not more than 1%) of the unreacted chitosan is washed with methanol and redissolved in water to remove the unreacted chitosan (water-insoluble) and then purified by way of precipitation from acetone or lyophilization to give the product (sulfonated chitosan).

Since the separation and refining steps of the above-described process are remarkably simple, they require less amount of solvents than those of the conventional process and improve the economical efficiency of the total process.

The sulfonated chitosan obtained by the above-described process is added solely or in combination with other additives in the form of dry powder or in a solution, for example, to the wood chips at the refining step with a disc refiner, or to the pulp slurry at the beating step before the papermaking step. The sulfonated chitosan is suitably used in an amount of 0.01-2% based on the bone-dry weight of the chips or the pulp. This addition of sulfonated chitosan enables power consumption to be remarkably reduced in the refining or beating step.

Depending on cases, other additives conventionally used in papermaking such as fillers, aluminum sulfate, sizing agents, dry strength resins, wet strength resins, retention aids, drainage aids or dyes may be added to the pulp obtained with the use of sulfonated chitosan to produce various types of paper or paperboard. If necessary, starch, polyvinyl alcohol, dyes, coating colors, surface sizing agents, anti-slipping agents or the like may be applied by using a size press, a gate roll coater, a bill blade coater or a calender. Examples of papers to which the present invention is applicable include coat base paper, printing or writing paper, information paper, medium grade (i.e. ground wood containing) printing paper, wrapping paper, sanitary paper and newsprint paper. Examples of paperboards include liner, corrugating medium, white board and gypsum liner board. These papers or paperboards made from the pulp obtained with the use of sulfonated chitosan in accordance with the present invention exhibit excellent paper strength.

Now the invention will be illustrated by way of referential, comparative referential and working examples. The below-described referential examples relate to the preparation of sulfonated chitosan wherein the C3/C6-positions are selectively sulfonated. These examples should be taken as illustrative and not in a limiting sense.

Referential Example 1

<Preparation of chitosan-3,6-sulfate>

5 <Pretreatment of chitosan>

Chitosan (a commercial product supplied by Tokyo Kasei Kogyo Kabushiki Kaisha) was treated with a 40% NaOH solution for four hours at 95°C and a purified chitosan (degree of deacetylation: 87.2%) was obtained after two-cycle repetition of filtration and neutralization. 5g of the purified chitosan was dissolved in 20g of a 2% aqueous solution of acetic acid and precipitated by neutralization with a 2% NaOH aqueous solution under agitation. The regenerated chitosan was washed with water and then with methanol and thereafter immersed in DMF for 3 hours and pressed. Thus a pretreated chitosan was obtained.

15 <Preparation of sulfonating agent>

24.5g of SO_3 was dissolved in 22.4g of DMF to form 46.9g of SO_3 -DMF complex.

<Synthesis of sulfonated chitosan>

20 46.9g of SO_3 -DMF complex (above-described) was dissolved in 200g of benzene. The total amount of the pretreated chitosan was added to the solution and the solution was stirred for 1 hour at room temperature. The settling was separated by filtration, washed with a small amount of methanol, dissolved in water and filtered. The filtrate is lyophilized and 8.3g of sulfonated chitosan was obtained. The degree of sulfonation was determined to be 1.12 (substitution degree) by elemental analysis and the yield based on chitosan was 98.4%.

25 It is confirmed by IR and ^{13}C -NMR that the obtained sulfonated chitosan is chitosan-3,6-sulfate wherein the C3 and C6-position hydroxyl groups are selectively and partially sulfonated and the C2-position NH_2 group is not sulfonated.

Referential Example 2

30 <Preparation of chitosan-3,6-sulfate hydrolysate>

Two grams of chitosan-3,6-sulfate obtained in the Referential Example 1 was dissolved in 300ml of 0.1N sulfuric acid aqueous solution. The solution was heated to 80°C for an hour to hydrolyze the chitosan-3,6-sulfate. Then the solution was neutralized in an ice bath with 30ml of a cooled 1N NaOH aqueous solution of 10°C, subjected to dialysis to remove the formed salt, concentrated at 40°C under reduced pressure and lyophilized to give 1.6g of chitosan-3,6-sulfate hydrolysate.

Referential Example 3

40 <Preparation of chitosan-6-sulfate>

<Pretreatment of chitosan>

Pretreated chitosan was obtained in the same manner as in Referential Example 1.

45 <Preparation of sulfonating agent>

35.7g of chlorosulfonic acid was added dropwise in 22.4g of DMF below 40°C to form 58.1g of ClHSO_3 -DMF complex.

50 <Synthesis of sulfonated chitosan>

58.1g of ClHSO_3 -DMF complex (above-described) was dissolved in 200g of benzene. The total amount of the pretreated chitosan was added to the solution and stirred for 3 hours at 50°C. The settling was separated by filtration, washed with a small amount of methanol, dissolved in water and filtered. The filtrate was lyophilized and 7.68g of sulfonated chitosan was obtained. The degree of sulfonation was determined to be 0.88 (substitution degree) by elemental analysis and the yield based on chitosan was 99.5%.

It is confirmed by IR and ^{13}C -NMR that the obtained sulfonated chitosan is chitosan-6-sulfate wherein the C6-position hydroxyl group is selectively and partially sulfonated and the C3-position hydroxyl group and C2-position NH_2

gr up are n t sulfonated.

Referential Example 4

5 <Preparation of chitosan-6-sulfate hydrolysate>

Chitosan-6-sulfate hydrolysate was obtained by repeating the process of Referential Example 2 except that chitosan-6-sulfate obtained in Referential Example 3 was used.

10 Referential Comparative Example

<Preparation of chitosan-N,3,6-sulfate wherein C3 and C6-position hydroxyl groups as well as C2-position amino group are sulfonated>

15 <Pretreatment of chitosan>

Chitosan (a commercial product supplied by Tokyo Kasei Kogyo Kabushiki Kaisha) was treated with a 40% NaOH solution for four hours at 95°C and a purified chitosan (degree of deacetylation: 87.2%) was obtained after two-cycle repetition of filtration and neutralization. 5g of the purified chitosan was soaked in 100ml of DMF at room temperature for 24 hours and thereafter pressed to remove the liquid so that the total weight was 10g. The chitosan was then subjected to the sulfonating treatment.

<Preparation of sulfonating agent>

25 24.5g of SO₃ was dissolved in 22.4g of DMF to form 46.9g of SO₃-DMF complex.

<Synthesis of sulfonated chitosan>

30 46.9g of SO₃-DMF complex (above-described) was dissolved in 200g of DMF. The total amount of the pretreated chitosan (above-described) was added to the solution and stirred for 1 hour at room temperature. 240g of methanol and 80g of 10N NaOH were added thereto and the settling was separated by filtration, washed with a large amount of methanol, dissolved in water and filtered. The filtrate was subjected to dialysis to remove sodium sulfate and methanol, concentrated and lyophilized and 5.7g of sulfonated chitosan was obtained. The degree of sulfonation was determined to be 1.17 (substitution degree) by elemental analysis and the yield calculated therefrom was 66.4%.

35 It is confirmed by IR and ¹³C-NMR that the obtained sulfonated chitosan is chitosan-N,3,6-sulfate wherein the not only C3 and C6-position hydroxyl groups but also the C2-position NH₂ group are partially sulfonated.

Example 1

40 <Refining assisting effect of sulfonated chitosan>

Samples of water-containing unbeaten and bleached softwood Kraft pulp provided from a paper mill were taken so that the bone-dry weight thereof might be 15g and water was added thereto to adjust the pulp concentration to be 15%. Sulfonated chitosans of the above Referential Examples 1-4 and Referential Comparative Example and Congo Red (comparative example) were respectively added thereto in an amount of 1% based on the pulp weight. The thus prepared pulps were beaten with a PFI mill under the following conditions:

Temperature: 20°C

Beating pressure: 1.8kg/cm²

50 Clearance: 0.4mm.

When the rotation number reached the predetermined value, the pulp was taken out of the mill and the freeness thereof was measured by using the Canadian standard freeness tester. A control pulp without additives was also beaten with a PFI mill in the same manner except that no additives were used and the freeness thereof was measured. The results are summarized in Table 1.

As is shown in Table 1, chitosan-3,6-sulfonate hydrolysate exhibits the most excellent refining assisting effect. The freeness achieved by 6,000 rotations with the use thereof is almost equivalent to that by 8,000 rotations with no additives. In the case that the C2 position amino group is sulfonated (Referential Comparative Example), only little improvement

in the refining assisting effect was observed in comparison with the case where no additives were used.

TABLE 1
Refining Assisting Effect of Sulfonated Chitosan

No.	Additive	Freeness (ml)		
		Rotation Number of PFI Mill		
		4000	6000	8000
1	No additive ¹⁾	580	470	370
2	Congo Red ²⁾	490	375	285
3	C-N,3,6-S ³⁾	560	460	370
4	C-3,6-S ⁴⁾	520	420	340
5	C-3,6-S(h) ⁵⁾	510	380	290
6	C-6-S ⁶⁾	535	435	360
7	C-6-S(h) ⁷⁾	520	410	320

NOTES:

- 1) Control
- 2) Comparative Example
- 3) Chitosan-N,3,6-sulfate (Referential Comp. Ex.)
- 4) Chitosan-3,6-sulfate (Product of Ref. Ex. 1)
- 5) Chitosan-3,6-sulfate hydrolysate
(Product of Ref. Ex. 2)
- 6) Chitosan-6-sulfate (Product of Ref. Ex. 3)
- 7) Chitosan-6-sulfate hydrolysate
(Product of Ref. Ex. 4)

Example 2

<Paper strength improving effect of sulfonated chitosan>

A beaten pulp having a freeness of around 370ml was selected from the pulp obtained in Example 1 and each of them was taken so as to contain 6g of pulp in bone-dry weight. Each sample was macerated for 10 minutes with 1.5 liters of water. Water was added thereto to make the total volume 2 liters and the mixture was made into paper having a basis weight of 60.0 ± 1.0 g/m² at pH 6.2. The papermaking was carried out in accordance with the TAPPI standard method by using a standard cylinder paper machine followed by wet pressing of 5min-3.9kg/cm² and 2min-3.5kg/cm². The thus obtained paper was subjected to humidity conditioning at 20°C and RH 65% for 24 hours and to the bursting strength test and the tensile strength test as specified in JIS (Japanese Industrial Standard) P 8112 and B113 respectively. The results (burst factors and breaking lengths) are summarized in the following Table 2.

TABLE 2**Paper Strength Improving Effect of Sulfonated Chitosan**

5

<u>No.</u>	<u>Additive</u>	<u>Freeness(ml)</u>	<u>Dry</u>	<u>Dry Breaking</u>
			<u>Burst Factor</u>	<u>Length (km)</u>
10 1	No additive ¹⁾	370	5.90	6.73
2	Congo Red ²⁾	370	6.06	6.94
3	C-N,3,6-S ³⁾	370	6.30	7.65
<hr/>				
15 4	C-3,6-S ⁴⁾	380	6.40	7.80
5	C-3,6-S(h) ⁵⁾	375	6.60	8.35
6	C-6-S ⁶⁾	360	6.60	7.70
20 7	C-6-S(h) ⁷⁾	320	6.45	8.10

NOTES:

- 1) Control
- 25 2) Comparative Example
- 3) Chitosan-N,3,6-sulfate (Referential Comp. Ex.)
- 4) Chitosan-3,6-sulfate (Product of Ref. Ex. 1)
- 30 5) Chitosan-3,6-sulfate hydrolysate
(Product of Ref. Ex. 2)
- 6) Chitosan-6-sulfate (Product of Ref. Ex. 3)
- 35 7) Chitosan-6-sulfate hydrolysate
(Product of Ref. Ex. 4)

As shown in the results of these tests, the papers obtained by the refining with the use of sulfonated chitosan exhibited higher strength than those obtained without the use thereof. In particular, chitosan-3,6-sulfonate hydrolysate which exhibited the most excellent refining assisting effect also exhibited the most excellent effect in improving the paper strength.

Recently, energy saving in production industries is required not only for reducing the production cost but also for preserving the environment of the world. Manufacturing of paper is one of the most energy-consuming industries and efforts to recycle the thermal energy in papermaking has been successfully made. The power demand for mechanical steps therein, however, has not been significantly reduced and the reduction thereof is the current problem. Refining of woodchips or pulp is one of the typical power-consuming steps and the power reduction in this step is important. With the addition of sulfonated chitosan according to the present invention, power required in the refining can be reduced by about 25% compared with the conventional refining without additives. In addition, this refining assisting additive improves paper strength. These days, shortage of pulp sources invites degradation of the quality of pulp fibers and increases the mixing rate of the broke and consequently augments the necessity of the use of additives such as paper strength resin. Under the circumstances, the use of sulfonated chitosan having refining assisting and paper strength improving effects is, not only economically but also socially, very meaningful.

Claims

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1. A method for refining woodchips or beating pulps, wherein a sulfonated chitosan, which is selectively sulfonated at the C3/C6 positions and not sulfonated at the C2-position NH₂ group, is used.

2. A method according to claim 1, wherein a sulfonated chitosan, which is sulfonated at the C3 and the C6 positions and not sulfonated at the C2 position NH₂-group, is used.
3. A method according to claim 1, wherein a sulfonated chitosan, which is sulfonated only at the C6 position and not sulfonated at the C2 position NH₂ group, is used.

Patentansprüche

1. Verfahren zum Feinmahlen von Holzspänen bzw. Papiermassen, wobei ein sulfoniertes Chitosan, das selektiv in C₃-/C₆-Stellung, nicht jedoch an der NH₂-Gruppe in der C₂-Stellung sulfoniert ist, verwendet wird.
2. Verfahren nach Anspruch 1, wobei ein sulfoniertes Chitosan, das in C₃- und C₆-Stellung, nicht jedoch an der NH₂-Gruppe in der C₂-Stellung sulfoniert ist, verwendet wird.
3. Verfahren nach Anspruch 1, wobei ein sulfoniertes Chitosan, das nur in C₆-Stellung, nicht jedoch an der NH₂-Gruppe in der C₂-Stellung sulfoniert ist, verwendet wird.

Revendications

1. Procédé de raffinage des copeaux de bois ou des pâtes à papier, dans lequel est utilisé un chitosane sulfoné, qui est sulfoné de manière sélective aux positions C-3/C-6 et non pas sulfoné à la position C-2 du groupement NH₂.
2. Procédé selon la Revendication 1, dans lequel est utilisé un chitosane sulfoné, qui est sulfoné aux positions C-3 et C-6 et non pas sulfoné à la position C-2 du groupement NH₂.
3. Procédé selon la Revendication 1, dans lequel est utilisé un chitosane sulfoné, qui est sulfoné uniquement à la position C-6 et non pas sulfoné à la position C-2 du groupement NH₂.